Radiochimica Acta 72, 7–17 (1996)
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Gas Phase Chemistry Experiments with Transactinide Elements*

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(Received June 13, 1995; revised August 10, 1995)

On-line gas chromatography / Transactinides / Rutherfordium (Element 104) / Hahnium (Element 105) / Relativistic effects

Abstract

In the past few years on-line gas chromatography has been successfully applied to separate volatile chlorides and bromides of element 104 (Rf = rutherfordium) and element 105 (Ha = hahnium) from heavy actinides. The volatility of these compounds was studied and compared with that of their lighter homologues under similar experimental conditions. The current article gives an overview about the predicted, relativistic and from empirical extrapolations expected chemical properties, it presents the latest experimental developments, the available experimental data on Rf and Ha halides, and discusses the analysis and the interpretation of these results in comparison with theoretical predictions.

1. Introduction

The special interest in the chemistry of the first transactinide elements 104 (Rf = rutherfordium) and 105 (Ha = hahnium), the heaviest elements studied to date using radiochemical techniques, is based on the expected influence of relativistic effects. At these very high atomic numbers the inner electrons of an atom are subjected to such large nuclear charges that they attain relativistic velocities. Relativistic effects are also felt by the valence electrons. Their more efficient screening from the nuclear charge leads to a stabilization of the spherical 7 *s* and 7 $p_{1/2}$ orbitals and a destabilization of the 6 *d* and 5 *f* orbitals. The modified atomic structure may strongly influence the chemical properties of the transactinides and their compounds. Recent relativistic calculations allow now detailed predictions of the chemical properties of the heaviest elements compared to their lighter homologues. Also, careful empirical extrapolations of the physicochemical properties of the transactinides and their compounds, exploiting the regularities in the groups and periods of the periodic table, are of great value in order to assess the significance of relativistic effects. However, these extrapolations cannot be regarded as purely "non-relativistic", since relativistic effects are present even in the lighter elements and are increasing down the columns of the periodic table.

Another reason for the interest in the chemical properties of the heaviest elements arised in conjunction with the recent discovery of two longer-lived neutron-rich isotopes of element 106 (Sg = seaborgium) [1], which seem to indicate the existence of the predicted new subisland of nuclear stability around $Z=108$ and $N=162$ [2]. The sensitivity of radiochemical methods may play an important role in discovering new transactinide isotopes and in determining their nuclear decay properties. In the center of this subisland spontaneous fission (SF) half-lives of about 10^8 s and α-decay half-lives in the order of seconds are predicted [2].

Unique chemical techniques had to be developed to experimentally study transactinide elements. The longest-lived known isotopes of Rf and Ha have half-lives of 78 s [3] and 34 s [4], respectively, and can currently be produced only on an "atom-at-the-time"-level in heavy ion fusion reactions with exotic target materials such as ^{248}Cm and ^{249}Bk. In these experiments also the question must be answered, whether the observed chemical behavior of single atoms or molecules has any connection to macroscopic physicochemical properties. Chemical studies of Lr and Rf in both aqueous and gas phases (see Refs. [5–12] for recent review articles) clearly indicate that the actinide series ends at Lr and the new 6 *d* transition series (the transactinide series) begins with Rf. The high volatility of the halides of the group 4 and 5 elements allows a fast gaschromatographic separation of transactinides from heavy actinides that are formed in transfer reactions with comparably high cross sections. First gaschromatographic experiments with transactinide elements were performed as early as 1966 by Zvara *et al.* [13]. In the past few years, using the so called OLGA (**O**n-**L**ine **G**as Chemistry **A**pparatus) technique [14], the volatility of Rf and Ha chlorides and bromides [3, 9, 15, 16] was reinvestigated. In comparison to experiments by Zvara *et al.*, the nuclear decay properties of the investigated radionuclides were registered directly after gaschromatographic separation, which allowed their unambiguous identification. From the experimentally determined retention behavior, adsorption enthalpies ($-\Delta H_a^{0(T)}$) on the chromatographic surface were determined for the chlorides and bromides of Rf and Ha, as well as for their lighter homologues, which were studied under similar experimental con-

* Presented at the symposium of the German Nuclear Chemistry Group at Berlin, September 1994.
In this article the element names endorsed by the Nomenclature Committee of the American Chemical Society for use in the US are employed.

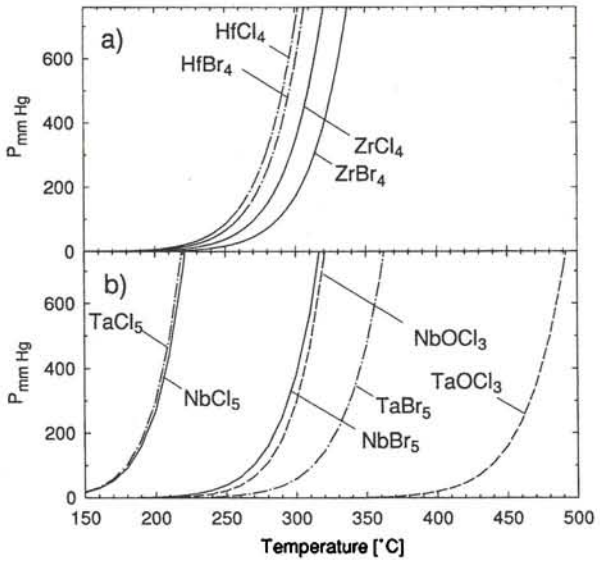

Fig. 1. Vapor pressure curves of the monomeric gas over the respective solids for a) $ZrCl_4$, $ZrBr_4$, $HfCl_4$, and $HfBr_4$, and b) $NbCl_5$, $NbBr_5$, $TaCl_5$, $TaBr_5$, $NbOCl_3$, and $TaOCl_3$, respectively.

ditions. A novel approach for the determination of $\Delta H_a^{0(T)}$ of the investigated species based on a microscopic model of gas-solid thermochromatography in open columns [17] was applied.

In the following, an overview about the predicted, relativistic and from empirical extrapolations expected chemical properties is given and the latest experimental developments are presented. The available experimental data of Rf and Ha halides, and the analysis and the interpretation of these results in comparison with theoretical predictions are discussed.

2. Halides and oxyhalides of the group 4 and group 5 elements

2.1 Chemical properties of Zr, Hf, Nb, and Ta halides and oxyhalides

Vapor pressure curves give a good measure of the relative volatility of compounds. In Fig. 1 the vapor pressure curves of the monomeric gas over the respective solids for Zr and Hf tetrachlorides and -bromides and for Nb and Ta pentachlorides and -bromides are shown, respectively. Also shown are the vapor pressure curves for Nb and Ta oxytrichlorides. The curves were calculated using tabulated standard sublimation enthalpies ($\Delta H_s^{0(298)}$) and standard sublimation entropies ($\Delta S_s^{0(298)}$) [18]. $HfCl_4$ and $HfBr_4$ are slightly more volatile than the Zr homologues, but less volatile than $TaCl_5$ and $NbCl_5$. Interestingly, the chlorides and bromides of Zr and Hf show about the same volatility, whereas $NbBr_5$ and $TaBr_5$ are considerably less volatile than their respective pentachlorides.

Not much is known about the ability of the group 4 elements to form oxyhalides. Morozov *et al.* [19] found that $ZrOCl_2$ and $HfOCl_2$ decompose to the tetrachloride and the oxide when heated and determined the vapor pressure curves of the tetrachlorides over their oxychlorides. Domanov *et al.* [20] observed that the deposition temperature of Zr and Hf changed, depending on the O_2 concentration in the reactive gas. A less volatile species was observed. In contrast to the group 5 oxychlorides, the oxychlorides of group 4 elements are expected to be less stable than the pure tetrachlorides and it is uncertain whether compounds such as $ZrOCl_2$ or $HfOCl_2$ exist in the gas phase. Nevertheless, the possibility of a transport reaction mechanism with the tetrachloride in the gas phase and the oxychloride in the adsorbed state should be considered in the interpretation of gas chromatography experiments [21].

Since in experiments with transactinide elements, only single molecules can be studied, $\Delta H_s^{0(298)}$ of e.g. $RfCl_4$ cannot be determined directly. Only $\Delta H_a^{0(T)}$ on the chromatographic surface (usually quartz) can be measured. However, it was demonstrated by Zvara *et al.* [22], that there exists a linear correlation between $\Delta H_a^{0(T)}$ and $\Delta H_s^{0(298)}$ for chlorides. By measuring $\Delta H_a^{0(T)}$ of chlorides of 24 elements on quartz surfaces, Eichler *et al.* [23] established the empirical expression:

$$-\Delta H_a^{0(T)} = (0.655 \pm 0.042) \cdot \Delta H_s^{0(298)} + (18.0 \pm 8.8) \quad \text{[kJ/mol]} \qquad (1)$$

2.2 Predicted chemical properties of Rf and Ha halides

In order to detect relativistic alterations of the chemical properties in transactinide elements and their compounds, the expected physicochemical properties must be predicted on the basis of theoretical calculations including relativistic corrections. But also, predictions based on extrapolations of periodic trends are invaluable, since these predictions account for relativistic alterations only in so far as these are already present in the lighter homologues. A comparison of the extrapolated physicochemical properties with the relativistic predictions can be regarded as an indicator for the presence of "relativistic effects".

Recently, relativistic calculations of the electronic structure of Rf were published. Glebov *et al.* [24], determined that the ground state of Rf should be a J = 2 level consisting of the $6d7s^27p$ configuration (80%) with a level only 0.5 eV higher for the $6d^27s^2$ configuration (95%), while the $7s^27p^2$ state is 2.9 eV above the ground state. Based on their calculations, Glebov *et al.* [24] concluded that despite the unusual ground state configuration Rf should show no distinctive *p*-character. In fact, Rf should behave similarly to Hf, a typical *d*-element. Johnson *et al.* [25], have confirmed the results of Glebov *et al.* [24], and have also calculated the first four ionization potentials of Rf and their respective radii. In a later publication some thermodynamic properties, like the enthalpies and Gibbs free

energies of formation for Rf-halides, and standard electrode potentials were calculated [26].

Using multiconfiguration Dirac-Fock (MCDF) calculations, Fricke *et al.* [27] calculated the electronic ground states for the group 5 elements V, Nb, Ta, and Ha in the charge states 0 to +5. In contrast to the calculated ground states for elements Lr ($7s^27p$) and Rf ($6d7s^27p$), a J = 3/2+ $6d^37s^2$ (87.1%) configuration resulted for the atomic ground state of Ha. The calculated MCDF ground states for Ha, Ha^+, Ha^{+2}, and Ha^{+3} differ from the respective ground states of homologous elements. They have more *s* and $p_{1/2}$ character due to relativistic effects. Fricke *et al.* [27] also presented values for the first five ionization potentials of all group 5 elements and ionic radii for the +2, +3, +4, and +5 ions of Ha.

Recently, the basic thermodynamic functions, the entropy, free energy, and enthalpy for Ha in electronic configurations d^3s^2, d^3sp, and d^4s^1 and for its +5 ionized state have been calculated as a function of temperature [28]. The calculations were based on the results of the calculations of the corresponding electronic states using the MCDF method.

The prediction of the volatility of transactinide halides is difficult, since there seems to be no direct correlation between electronic structure and macroscopic volatility. Pershina *et al.* [29] have developed a formalism which allows a coarse prediction of the volatility of a compound assuming that the volatility is determined by the attraction energy between two identical molecules. The dispersion interaction is governed by the effective charges on the ligands (which are compensated by an effective charge on the central metal atom). Furthermore, a measure of the covalency of the bonding in a compound (overlap population data) can be used as a criterion to predict the volatility. In performing relativistic molecular orbital calculations, several authors calculated the effective charges on the central metal atom in tetrachloride molecules of group 4 elements Ti, Zr, Hf, and Rf. Zhuikov *et al.* [30], have performed relativistic SCF-X_α scattering wave Dirac-Slater computations, whereas Ryzhkov *et al.* [31], and Pershina *et al.* [32] used the Dirac-Slater discrete variational method. In a series of previous articles Pershina *et al.* [29, 33] also calculated effective charges on the central metal atom in pentachloride and -bromide molecules of group 5 elements V, Nb, Ta, and Ha. They predicted a higher volatility of $HaBr_5$ compared to its lighter homologue compounds, due to the low effective charge of the metal atom. In analogy to the procedure described in [29], $\Delta H_s^{0(298)}(HaCl_5)$ and $\Delta H_s^{0(298)}(RfCl_4)$ were also calculated, using the effective charges on the ligands from Ref. [32].

Alternatively, the chemical properties of an unknown element and its compounds can be predicted by exploiting the fundamental relationships of the physicochemical data of the elements and their compounds within the groups and the periods of the periodic table. In employing these periodic trends, Eichler *et al.* [34, 35] extrapolated $\Delta H_s^{0(298)}(RfCl_4)$, $\Delta H_s^{0(298)}(HaCl_5)$, and $\Delta H_s^{0(298)}(HaBr_5)$.

The physicochemical properties of the group 4 and 5 pure chlorides and bromides and the group 5 oxychlorides, along with the predicted, relativistic, and, from periodic trends, extrapolated values for $\Delta H_s^{0(298)}$, $\Delta S_s^{0(298)}$, and vapor pressure parameters are summarized in Table 1. For $TaBr_5$ an unusually high $\Delta S_s^{0(298)}$ is tabulated which is probably due to a dimeric state in solid $TaBr_5$. For the calculation of the vapor pressure parameters, $\Delta S_s^{0(298)}(NbBr_5)$ was used. Generally, volatilities predicted from relativistic calculations are higher than from physicochemical properties extrapolated ones. Predictions for $RfBr_4$ are not yet available.

3. Experimental techniques

Using frontal gas chromatography with $ZrCl_4$ and $NbCl_5$ as chlorinating agents and carriers, Zvara *et al.* [13, 22, 36] detected a SF activity attributed to the decay of an isotope of element 104 at the exit of their column under conditions where Zr and Hf also rapidly passed through the chromatography apparatus. In later experiments they developed thermochromatography [37] to further study volatile Rf and Ha halides. In thermochromatography a longitudinal, negative temperature gradient is established in the chromatography column in the flow direction of the carrier gas. Volatile species are deposited in the column according to their volatility and form distinct deposition zones. Mica sheets inserted into the chromatography column served as fission track detectors. Thermochromatography, as a tool for investigating the chemistry of the transactinides, has a number of advantages, but also disadvantages. Advantages are the high speed at which the production of volatile halides and their separation occurs. The recoiling reaction products are rapidly swept from the site of the target to the entrance of the chromatography column, where halogenating agents are added. Transactinide nuclides decaying by SF are registered in the column and thus providing information about their volatility. Moreover, thermochromatography experiments are relatively easy to perform. However, there are also serious disadvantages. The fact that the position of the deposition zones of homologues can be measured only after completion of the experiment makes the interpretation of the relative volatility of the short-lived transactinides compared to the detected, much longer lived homologues difficult. In experiments with group 4 halides, the deposited short-lived radionuclides of Hf can be traced by means of its longer-lived lanthanide decedents which form non-volatile halides. In addition, SF is an unspecific decay mode of many heavy actinides and transactinides, which allows no identification of the decaying nuclide. Also, it is not possible to determine the half-life of the investigated nuclide.

In order to avoid these disadvantages, a different technique, the on-line isothermal gas chromatography

Table 1. Physicochemical properties of group 4 and 5 pure chlorides and bromides and the group 5 oxychlorides, along with the predicted, relativistic- and from periodic trends extrapolated values for Rf and Ha homologues

Molecule	T_m (°K)	T_b (°K)	$\Delta H_s^{0(298)}$ (kJ/mol)	$\Delta S_s^{0(298)}$ (J/mol K)	$\log p = A + BT^{-1}$ (mmHg)		Reference
					A	B	
$ZrCl_4$		609	110.5	186.1	12.60	−5771	[18]
$HfCl_4$		589	104.7	181.9	12.39	−5470	[18]
$RfCl_4$	–	–	107	–	–	–	relativistic [29, 32]
			122−138	–	–	–	extrapolated [34]
$ZrBr_4$	–	628	115.9	189.8	12.80	−6054	[18]
$HfBr_4$	–	597	109.5	188.8	12.74	−5720	[18]
$RfBr_4$	–	–	–	–	–	–	relativistic
			–	–	–	–	extrapolated
$NbCl_5$	479	519	94.0	190.1	12.81	−4911	[18]
$TaCl_5$	490	506	94.1	191.2	12.87	−4917	[18]
$HaCl_5$	–	–	85	–	12.8	−4446	relativistic [29, 33]
			94	192.1	12.91	−4921	extrapolated [34]
$NbBr_5$	527	634	112.5	190.5	12.83	−5875	[18]
$TaBr_5$	538	617	121.9	216.4[a]	12.83[b]	−6368	[18]
$HaBr_5$			97		12.5	−5088	relativistic [29]
			109−118	196.6	10.27	−5735...−6184	extrapolated [35]
$NbOCl_3$		607	128.5	216.3	14.18	−6712	[18]
$TaOCl_3$		600[c]	170.1	222.3	14.50	−8887	[18]
$HaOCl_3$	–	–	–	–	–	–	relativistic
			180	226.5	14.71	−9403	extrapolated [34]

[a] $\Delta S_s^{0(298)}$ high, probably because of dimeric molecules in solid state.
[b] Calculated with $\Delta S_s^{0(298)}(NbBr_5)$.
[c] Decomposition temperature.

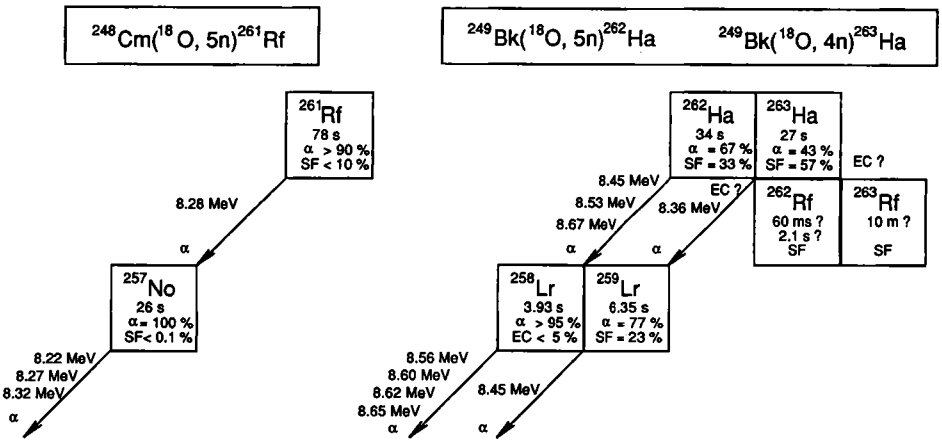

Fig. 2. Decay properties of ^{261}Rf and $^{262,263}Ha$ and their daughter activities.

was developed. In the past few years this technique was successfully applied to study the volatility of Rf and Ha halides [3, 9, 15, 16]. The transactinide nuclides ^{261}Rf and $^{262,263}Ha$ were produced via the $^{248}Cm(^{18}O, 5n)$ and the $^{249}Bk(^{18}O, 4,5n)$ heavy ion fusion reactions. The decay properties of the radionuclides ^{261}Rf [3, 38] and $^{262,263}Ha$ [4, 39, 40] are shown in Fig. 2. In Fig. 3 a schematic diagram of the OLGA technique is shown. In the target chamber (not shown), the recoiling reaction products are thermalized in helium loaded with aerosols (KCl, MoO_3, carbon) and, attached to the surface of the aerosols, continuously transported through a capillary to the OLGA setup. The same gas-jet transport system was used to study short-lived fission products from a ^{235}U target at a reactor neutron beam line. In the first section of the

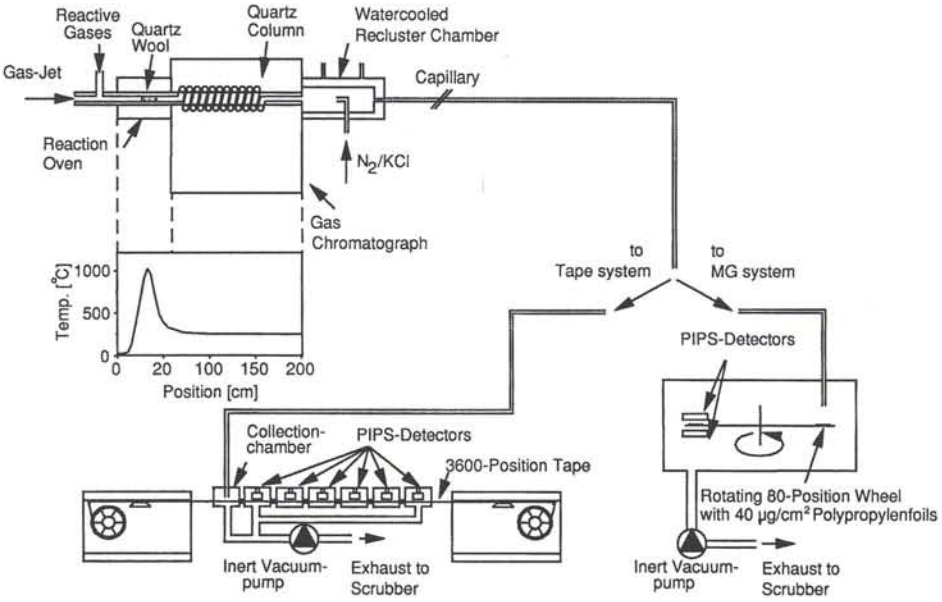

Fig. 3. Schematic diagram of OLGA III in combination with the tape detection system or the MG detection system (for details see text).

chromatography column, the reaction products are stopped on a quartz wool plug. This section is heated to 900−1000 °C. At the position of the quartz wool plug, halogenating agents such as HBr, BBr_3, HCl or Cl_2 are added. The second part of the quartz column serves as isothermal chromatography section. Volatile species, formed at the position of the quartz wool plug, are transported along the cooler chromatography section of the column by the carrier gas flow. The molecules undergo numerous sorption/desorption steps, with retention times indicative of their volatility at specific temperatures of the isothermal part of the column. Volatile products leaving the column through the tip are thermalized in the recluster chamber. Here, the products are reattached to new aerosol particles (Ar/KCl) for transport to the detection system.

Several versions of isothermal gas chromatography instruments were developed, all based on the same operation principle. The first device was OLGA II [14]. Later HEVI (**H**eavy **E**lement **V**olatility **I**nstrument) was built [41], which featured an increased chromatographic resolution due to longer columns and better isothermal temperature profiles. With both instruments, the time needed for separation and transport to detection was about 20 s, the time consuming process being the reclustering. Recently, a much faster version of an isothermal chromatography system, OLGA III [42], was developed. In the water-cooled recluster unit of only 15 cm^3 volume, the two gas streams meet head on. The turbulent mixing guarantees a fast cooling, and an efficient and stable attachment of the volatile compounds on the recluster aerosol. The residence time in the recluster unit was thus reduced by one order of magnitude. By using a 2 m long column inside a commercial gas chromatography oven, the chromatographic resolution was further improved.

Two detection systems are used, the MG (**M**erry-**G**o-round) rotating wheel [43] or the moving tape system [14]. In the MG system, the separated activities are deposited on thin polypropylene foils (30−40 µg/cm^2) at the periphery of an 80 position wheel. Successively, the wheel is stepped to move the collected activity between six pairs of PIPS (**P**assivated **I**mplanted **P**lanar **S**ilicon) detectors, which register α-particles and SF events from both sides of the sample. All events are registered in an event-by-event mode. To prevent interference from long-lived SF activities, the tape system was developed. Here, the activity is deposited at the collection site on a computer tape and subsequently stepped in front of 6 PIPS detectors. With these detection systems, the studied radionuclides were unambiguously identified after gas chromatographic separation via their half-lives and characteristic mother-daughter α-α correlations. In experiments with short-lived isotopes of elements Zr, Nb, Hf, and Ta the aerosols carrying the separated activities were retained on glass fiber filters and measured in front of a HPGe detector.

4. Monte Carlo analysis procedure

In a number of experiments the volatility of $ZrCl_4$ and $HfCl_4$ on quartz surfaces with trace amounts was studied. Usually thermochromatography experiments have been performed [20, 23, 36, 44, 45], but also on-line experiments with short-lived radionuclides have been carried out [3, 46−48]. In these experiments a lower volatility of $ZrCl_4$ and $HfCl_4$ compared to $NbCl_5$ was determined, as expected. However, depending on the analysis procedure and the selected standard state, $\Delta H_a^{0(T)}$-values varying from −74 to −98 kJ/mol resulted for e.g. $ZrCl_4$. Similarly, in experiments with

$NbCl_5$ and $NbOCl_3$ [16, 20, 23, 45, 46, 48–51], values between −66 kJ/mol and −88 kJ/mol for $\Delta H_a^{0(T)}(NbCl_5)$ and between −74 kJ/mol and −99 kJ/mol for $\Delta H_a^{0(T)}(NbOCl_3)$ were reported, respectively. It is therefore not possible to draw conclusions about the relative volatility of compounds from different experiments solely based on $\Delta H_a^{0(T)}$-values.

Clearly, a standard analysis procedure has to be adopted, which yields consistent results, independently of the experimental set-up. In addition, it would be desirable to also reanalyze older experiments. A novel approach for determining $\Delta H_a^{0(T)}$ of the investigated species was proposed by Zvara [17]. On the basis of a microscopic model of gas-solid thermochromatography in open columns a Monte Carlo code was developed [52], which allowed to generate thermochromatographic deposition zones, as well as to describe yield curves observed in isothermal chromatography experiments. This model is well suited to accommodate the influence of high carrier gas flow rates, the actual temperature profiles in the column, and to account for the different half-lives of the investigated species. The microscopic migration of a molecule in the column is replaced by a series of sorption/desorption events with no change in coordinate, followed by an effective random downstream displacement. It is assumed, that mostly the displacements between two collisions of a molecule with the wall are small, and that only rarely the molecule diffuses far enough from the wall to be carried downstream by the carrier gas flow. Thus, the actual number of displacements is greatly reduced, allowing the simulation of many molecules ($>10^4$) within reasonable time. The adsorption residence time is governed by the Frenkel equation. The recommended value for τ_o (period of oscillations of the molecule in the adsorbed state perpendicular to the surface) for quartz surfaces is 2×10^{-13} s [53].

The applicability of the Monte Carlo model is illustrated by analyzing a recent thermochromatography experiment on the bromides of Hf and Rf by Zvara *et al.* [54]. After completion of the experiment, fission tracks, as well as ^{165}Tm (a long-lived descendent of ^{165}Hf), were found in the section with the longitudinal temperature gradient after completion of the experiment. In assuming that element 104 would form volatile bromides like its lighter homologues Zr and Hf, the fission tracks were attributed to the SF decay of ^{259}Rf, which was produced in the reaction ^{242}Pu + ^{22}Ne. In the upper part of Fig. 4, the measured deposition profile for ^{165}Tm (^{165}Hf) and the registered 46 SF decays are shown. The SF-events are distributed over almost the entire length of the column and form no distinct deposition peak. In the lower part the integrated distributions are shown. Solid lines indicate the predicted distributions from the Monte Carlo model. Each profile was simulated with 10^4 molecules. The model accurately describes the observed distribution for ^{165}Tm (^{165}Hf), $\Delta H_a^{0(T)}(HfBr_4)$ = −86 kJ/mol was determined. In employing the quoted half-life of ^{259}Rf of 4.5 s [54], a good agreement with the observed distribution was achieved and $\Delta H_a^{0(T)}(RfBr_4)$ = −68 kJ/mol was obtained. By distributing the 46 registered SF-events in 500 simulated experiments, also the 3 σ error limit on the calculated distribution could be established. Applications of the Monte Carlo model to isothermal chromatography experiments will be discussed in the following section.

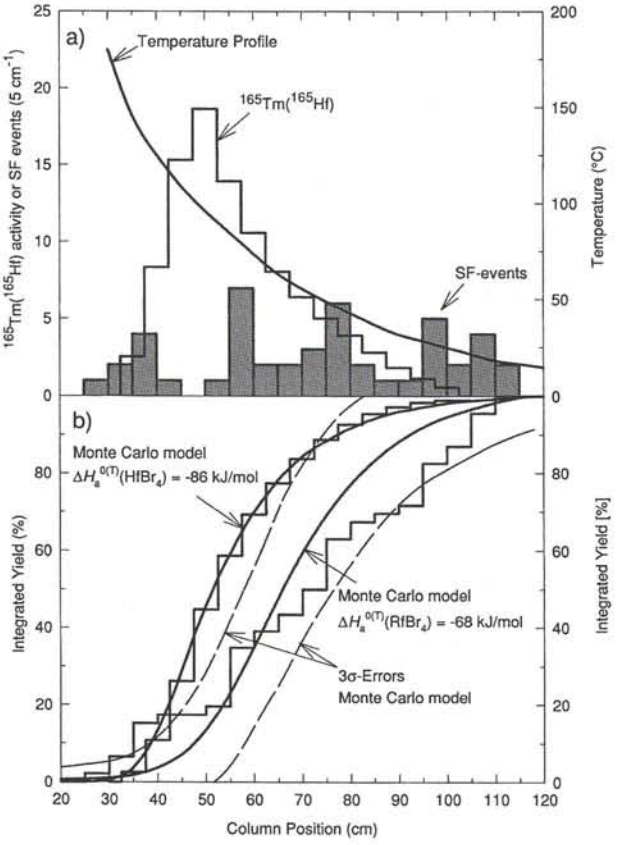

Fig. 4. Results of a typical thermochromatography experiment [54] and the corresponding Monte Carlo analysis. a) Temperature gradient, measured deposition profile of ^{165}Tm (^{165}Hf), and registered SF decays attributed to the decay of ^{259}Rf. b) Integrated distributions and the distributions from the Monte Carlo calculations.

5. On-line isothermal gas chromatography experiments with Rf and Ha

5.1 Experiments with Rf

In 1990 Türler *et al.* [9] studied the volatilities of chlorides and bromides of elements Hf and Rf using OLGA II. They detected α-particles from the decay of 78-s ^{261}Rf and its 26-s daughter ^{257}No and registered a number of α-α correlations that unambiguously proved that indeed element 104 (Rf) formed volatile halides. They determined a higher volatility for Rf-bromides than for the lighter Hf homologues and found a high volatility for Rf-chlorides. A comparison of this data with the data of Zvara *et al.* [13, 22, 36] had to consider the fact that the experiments by Türler *et al.* employed a KCl aerosol gas-jet to transport the activity from the target to the chromatography apparatus. At

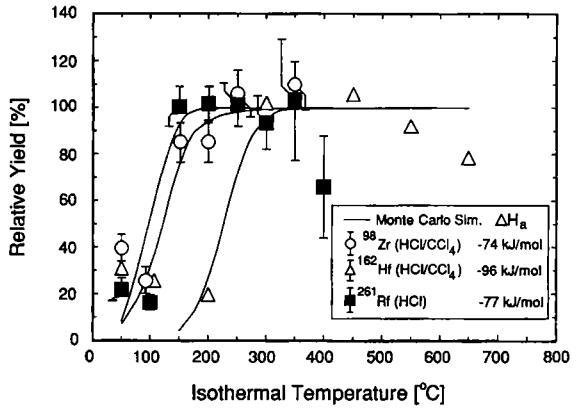

Fig. 5. Relative yields measured with HEVI for chlorides of Zr, Hf, and Rf as a function of isothermal column temperature (data from [48]).

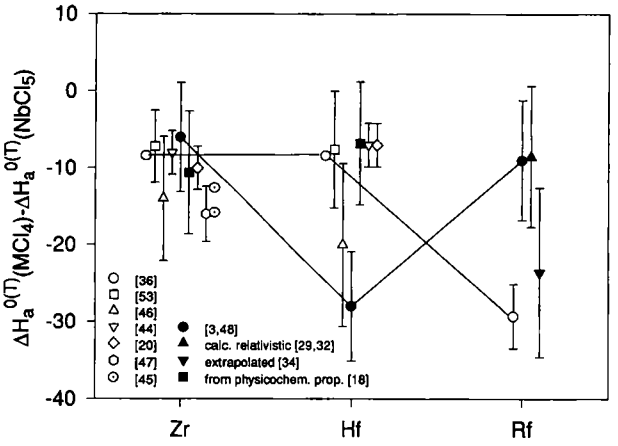

Fig. 6. $\Delta H_a^{0(T)}$-values on quartz surfaces for chlorides of Zr, Hf, and Rf relative to $\Delta H_a^{0(T)}(NbCl_5)$ from various sources.

the end of the experiments parts of the insides of the quartz columns were covered with visible amounts of KCl. It is therefore possible that the chromatography took place on a KCl surface and not on a pure SiO_2 surface as this was the case in Zvara's work. In addition the formation of compounds of the type K_2RfCl_6 had to be considered.

In a succeeding experiment employing HEVI [41], the volatility of Rf-chlorides and its lighter homologues was studied in more detail by Kadkhodayan *et al.* [3, 48]. In these experiments a MoO_3 aerosol gas-jet was used to transport the activities from the target recoil chamber to the chromatography apparatus. The MoO_3 cluster material forms very volatile oxychlorides and thus, compared to KCl aerosols, does not deposit inside the chromatography column. A total of 837 α-particles attributed to the decay of ^{261}Rf and its daughter ^{257}No were detected after the chromatography apparatus. A half-life of 78^{+11}_{-6} s resulted for the decay of ^{261}Rf, in good agreement with the 65^{+10}_{-10} s literature value [38]. The relative yields measured at each isothermal temperature for chlorides of ^{98}Zr, ^{162}Hf, and ^{261}Rf under similar experimental conditions are shown in Fig. 5. Chlorinating agents were 100 ml/min HCl in experiments with Rf and HCl saturated with CCl_4 vapors in experiments with Zr and Hf. The experiments were analyzed using the Monte Carlo model.

In order to compare the results of Kadkhodayan *et al.* [3, 48] with literature data, the adsorption enthalpies resulting from different analysis procedures had to be evaluated. Fortunately, in most of the experiments on the volatility of group 4 halides, also $\Delta H_a^{0(T)}(NbCl_5)$ was determined with the same experimental setup. By comparing $\Delta H_a^{0(T)}(ZrCl_4)$ relative to $\Delta H_a^{0(T)}(NbCl_5)$, inconsistencies resulting from different analysis procedures were eliminated (Fig. 6). The maximum spread of the $\Delta H_a^{0(T)}(ZrCl_4)$ values of 34 kJ/mol thus reduced to less than 9 kJ/mol. All authors reported $ZrCl_4$ being less volatile than $NbCl_5$. Differences in adsorption enthalpy ranged from about -7 to -16 kJ/mol. A similar situation is observed for $HfCl_4$. Using relation [1], and the $\Delta H_s^{0(298)}$-values from Table 1 expected adsorption enthalpy differences of -10.6 kJ/mol and -6.8 kJ/mol resulted for macroscopic amounts of $ZrCl_4$ and $HfCl_4$, respectively. These values are in good agreement with the data obtained with tracer quantities and from carrier-free experiments.

Within the error limits the volatility of $ZrCl_4$ relative to $NbCl_5$ determined in the work of Kadkhodayan *et al.* [3, 48] agrees with other studies. However, for $HfCl_4$ a much lower volatility was observed, even though the experimental conditions were kept as similar as possible to the $ZrCl_4$ experiments. It is not clear if Hf is more susceptible to traces of impurities in the system (O_2, H_2O) and thus behaved in a manner as observed by Domanov *et al.* [20] or if Hf reacted in some way with the MoO_3 transport aerosol.

Within the error limits $RfCl_4$ exhibits about the same volatility as $ZrCl_4$ or $HfCl_4$ and thus shows the volatility expected from relativistic calculations. From extrapolations one would expect a slightly less volatile $RfCl_4$.

These results can now be also compared with the results from Zvara *et al.* [36]. If the experiments are reanalyzed with the correct half-life of ^{259}Rf, adsorption enthalpies between -24 and -26 kcal/mol resulted [55]. The volatility of $RfCl_4$ chloride determined in these experiments is about -25 kJ/mol to -33 kJ/mol lower than for $NbCl_5$. Interestingly, Rf exhibits about the same, lower volatility as does Hf in the work of Kadkhodayan *et al.* [3, 48].

5.2 Experiments with Ha

First experiments using the ^{249}Bk(^{18}O, 4,5n) reaction to produce the longer lived isotopes of Ha ($34^{+4.6}_{-4.6}$-s ^{262}Ha [4] and 27^{+10}_{-7}-s ^{263}Ha [40]) and the OLGA II setup [14, 56] were described by Gäggeler *et al.* [57] who studied the volatility of group 5 bromides using HBr and BBr_3 as brominating agents. In conjunction with the MG rotating wheel detection system, α-particles

and SF events were measured after the chromatography column. A decay curve analysis of the detected α-particles in the energy range from 8.35 to 8.73 MeV yielded a half-life of 33 ± 6 s in agreement with the literature value for ^{262,263}Ha [4, 40]. Two possible α-α correlations from the decay of the ^{262}Ha-^{258}Lr mother daughter pair were registered. However, from the total of the detected α-particles in the energy range from 8.35 to 8.73 MeV, far too few α-α correlations were found. The volatility of hahnium-bromides was found to be intermediate between those of niobium- and tantalum-bromides. The data points for hahnium-bromides have large errors due to poor statistics.

A second series of experiments to study the volatility of group 5 bromides was conducted [15] using a moving tape detection system [14, 58]. Unfortunately, a higher contamination of the ^{249}Bk target with Pb, which produced unwanted Po activities compared to the previous experiments, prevented the detection of α-α correlations. The determination of the yield of ^{262,263}Ha was accomplished by measuring the SF decays of these isotopes. From the sum of all gas chemistry experiments, a half-live of 44^{+19}_{-12} s was determined for the SF activity, which, within the error limits, was consistent with the literature values for ^{262,263}Ha [4, 40]. The volatility of $TaBr_5$ was studied much more carefully than in previous experiments and was found to be similar to that of $NbBr_5$. Interestingly, volatile bromides of Nb and Ha were obtained by using HBr as brominating agent, whereas volatile Ta bromides were only formed when the HBr was saturated with BBr_3 vapors. From these experiments the adsorption enthalpies of the group 5 bromides were evaluated. The trend in volatility was Nb$\approx$Ta$>$Ha.

In 1992, the volatility of group 5 chlorides, using HEVI [41] and the tape detection system was studied. The nuclides ^{262,263}Ha were produced in the ^{249}Bk (^{18}O, 4,5n) reaction at the GSI UNILAC accelerator in Darmstadt. Unfortunately, these experiments were hampered by low gas jet efficiencies and only preliminary results are available [48, 59]. A decay curve analysis of SF activities observed in all gas chemistry runs at a beam energy of 99 MeV resulted in a half-life of 47^{+11}_{-8} s, assuming a minor contamination with ^{256}Fm(^{256}Md). This half-life was somewhat long compared to the literature values for ^{262,263}Ha [4, 40], but agreed well with the 44^{+19}_{-12} s half-life observed in earlier gas-chemistry experiments [15]. The analysis of α-spectra revealed 7 correlated α-α pairs, which resulted from the decay of 34-s ^{262}Ha and its 3.93-s ^{258}Lr daughter [60]. Half-lives of 28^{+17}_{-8} s and $3.8^{+2.3}_{-1.0}$ s resulted for the mother and daughter nuclides, respectively, in good agreement with the literature values [4, 60]. The chemical yield of Ha-chlorides at 250 °C and higher isothermal temperatures was considerably higher than the one measured at 80 °C. This indicates that Ha-chlorides are more volatile than their respective bromides, probably similar in volatility to $NbCl_5$. It is interesting to note that despite the use of various chlorinating agents including Cl_2, a highly volatile

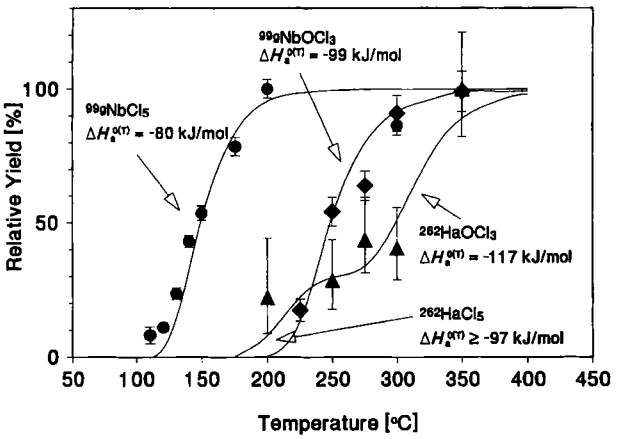

Fig. 7. Relative yields measured with OLGA III for ^{262}Ha-chlorides as a function of isothermal column temperature compared to $^{99g}NbCl_5$ and $^{99g}NbOCl_3$ [16].

$TaCl_5$, similar in volatility to $NbCl_5$ was not observed [48]. A less volatile Ta-species probably $TaOCl_3$ was observed, for which an adsorption enthalpy of -153 ± 11 kJ/mol was determined.

The most recent experiments on the volatility of Ha-chlorides using OLGA III were performed 1993 at Lawrence Berkeley Laboratory at the 88-Inch cyclotron [16]. Again the ^{249}Bk(^{18}O, 4,5n) reaction was used to produce ^{262,263}Ha. The data analysis revealed 27 α-α correlations in a 20 s correlation time window. Considering all possible sources, about 5 random correlations not originating from the decay of ^{262}Ha and its ^{258}Lr daughter had to be expected. The decay curve analysis yielded half-lives of $22.0^{+4.3}_{-3.5}$ s for the mother and $6.8^{+2.2}_{-1.5}$ s for the daughter nuclide. Also a total of 54 coincident (simultaneous detection of both fragments in the top- and the bottom detector) SF events were registered. A maximum likelihood decay curve fit [61] to the recorded life times, assuming a minor ^{256}Fm contamination yielded a half-life for ^{262}Ha of $21.0^{+4.9}_{-4.5}$ s and a ^{256}Fm contribution of 16% (8.6 SF-events). The half-life for ^{262}Ha was in agreement with the half-life determined from the α-α correlation analysis, but too short compared to the literature value of $32.6^{+6.5}_{-6.5}$ s [4]. Compared to earlier experiments the SF half-life was considerably shorter, indicating a better separation from ^{256}Fm.

The conditions at which the experiments were conducted, were as near as possible to the conditions where $^{99g}NbCl_5$ was separated in the test experiments at the PSI SAPHIR reactor [16]. In order to reduce the free O_2 partial pressure as far as possible, carbon aerosols, generated by spark discharge, were used to transport the activity from the target to the chemistry apparatus. As chlorinating agent HCl purified with activated charcoal at 900 °C at a flow rate of 100 to 200 ml/min was added. The relative yield curve for Ha-chlorides consisting of both α-α correlations and SF yields is shown in Fig. 7 [16]. Also shown are the yield curves measured for 15-s $^{99g}NbCl_5$ and

Table 2. Experimentally determined physicochemical properties of group 5 pentachlorides, oxytrichlorides and pentabromides compared to literature data and predicted relativistic and from periodic trends extrapolated values

Supposed species	$-\Delta H_a^{0(T)}$ (kJ/mol)	$\Delta H_s^{0(298)c}$ (kJ/mol)	$\Delta H_s^{0(298)d}$ (literature) (kJ/mol)	$\Delta H_s^{0(298)e}$ (relativistic) (kJ/mol)	$\Delta H_s^{0(298)f}$ (extrapolated) (kJ/mol)
$NbCl_5$	-80 ± 1^a	95 ± 16	94.0		
$NbOCl_3$	-99 ± 1^a	124 ± 16	128.5		
$HaCl_5$	$\geq-97^a$	≤120		85	94
$HaOCl_3$	-117 ± 3^a	152 ± 18			180.0
$NbBr_5$	-93 ± 4^b	115 ± 18	112.5		
$TaBr_5$	-101 ± 4^b	127 ± 18	121.9		
$HaBr_5$				97	109–118
$HaOBr_3$	-121 ± 11^b	158 ± 25			

[a] Data from Ref. [16].
[b] Reanalyzed experimental data from Ref. [15].
[c] Calculated using equation (1).
[d] Values from Ref. [18].
[e] Predicted values from relativistic calculations [29, 33].
[f] Extrapolated values from [34, 35].

$^{99g}NbOCl_3$. The yield curves were analyzed with the Monte Carlo model. The shapes of the calculated yield curves reproduced the measured yield curves very well. The resulting $\Delta H_a^{0(T)}$-values are given in Table 2. The yield curve for Ha-chlorides was analyzed assuming that two chemical species were present, namely $HaCl_5$ and $HaOCl_3$. Compared to $NbOCl_3$, $HaOCl_3$ became volatile at an approximately 50 °C higher temperature, whereas for the volatility of $HaCl_5$ only a lower limit was established.

In Table 2, the experimentally determined $\Delta H_a^{0(T)}$-values of group 5 pentachlorides, oxytrichlorides from [16] and pentabromides from [15] were converted to $\Delta H_s^{0(298)}$-values using equation (1) and compared to literature data and predicted relativistic and from periodic trends extrapolated values. In order to allow a comparison of chlorides and bromides, the data from [15] has been reanalyzed using the Monte Carlo model. It was assumed that relation (1) is also applicable to bromides. The resulting $\Delta H_s^{0(298)}$-values for $NbCl_5$ and $NbOCl_3$, as well as those for $NbBr_5$ and $TaBr_5$ were in good agreement with the literature data. The experimental upper limit of 120 kJ/mol for $\Delta H_s^{0(298)}$ ($HaCl_5$) was not in contradiction with the relativistic calculations and with the extrapolated values. With both methods, $HaCl_5$ is expected to be equally or more volatile than $NbCl_5$. As predicted by the classical extrapolations, a less volatile $HaOCl_3$ compared to $NbOCl_3$ was observed. Unfortunately, measurements of Ta-chlorides with OLGA III are still lacking.

6. Conclusions

The experimental verification of relativistic effects proves to be a difficult task, since the volatility measurements require a high degree of accuracy. The difference of $\Delta H_a^{0(T)}$ from classical extrapolations and from relativistic calculations are smaller than anticipated. There are large errors associated with the theoretical predictions, as well as with the experimental data. In an ideal experiment short-lived activities of all of the elements in a group should be simultaneously produced and their relative volatility determined. In addition, the influence of oxygen and oxygen containing impurities needs to be carefully studied. More accurate calculations are needed to predict the volatility of a compound from its electronic structure. Therefore, the van der Waals interactions of a molecule with a surface site need to be evaluated.

Nevertheless, the results of on-line gas chemistry experiments of the past years have shown that a continuous, fast and efficient separation of single atoms of transactinide nuclides is possible. This is especially encouraging since the elements of groups 6 and 7 are also known to form volatile halides and oxyhalides. The separated nuclides were unambiguously identified by measuring their nuclear decay properties. The high sensitivity of chemical methods combined with sophisticated detection systems, may allow the discovery of new heavy isotopes of elements 106 (Sg = seaborgium) and 107 (Ns = Nielsbohrium).

The application of a Monte Carlo model to determine $\Delta H_a^{0(T)}$ was very successful and allows to establish the statistical significance of experiments with few separated nuclides. In addition, the model will help to evaluate results from older experiments and predict optimum experimental conditions in future experiments. It was demonstrated that an empirical relation between $\Delta H_a^{0(T)}$ and $\Delta H_s^{0(298)}$ exists for chlorides. This way, the predicted $\Delta H_s^{0(298)}$ can be compared with experimental results. By using this relation the identification of the investigated compound can be accomplished for the homologues of transactinide halides. However, it would be highly desirable to also be able to determine directly the chemical composition of transactinide halide compounds, for instance by coupling a mass spectrometer to the gas chromatography system.

References

1. Lazarev, Y. A., Lobanov, Y. V., Oganessian, Y. T., Utyonkov, V. K., Abdullin, F. S., Buklanov, G. V., Gikal, B. N., Iliev, S., Mezentsev, A. N., Polyakov, A. N., Sedykh, I. M., Shirokovsky, I. V., Subbotin, V. G., Sukhov, A. M., Tsyganov, Y. S., Zhuchko, V. E., Lougheed, R. W., Moody, K. J., Wild, J. F., Hulet, E. K., McQuaid, J. H.: Phys. Rev. Lett. **73**, 624 (1994).
2. Patyk, Z., Sobiczewski, A.: Nucl. Phys. **A533**, 132 (1991).
3. Kadkhodayan, B., Türler, A., Gregorich, K. E., Czerwinski, K. R., Eichler, B., Gäggeler, H. W., Hamilton, T. M., Hannink, N. J., Jost, D. T., Kacher, C. D., Kovacs, A., Kreek, S. A., Lane, M. R., Mohar, M. F., Neu, M. P., Sylwester, E. R., Lee, D. M., Nurmia, M. J., Seaborg, G. T., Hoffman, D. C.: submitted to Radiochim. Acta.
4. Bemis, Jr., C. E., Ferguson, R. L., Plasil, F., Silva, R. J., O'Kelly, G. D., Kiefer, M. L., Hahn, R. L., Hensley, D. C., Hulet, E. K., Lougheed, R. W.: Phys. Rev. Lett. **39**, 1246 (1977).
5. Schädel, M.: Inst. Phys. Conf. Ser. **No. 132**, 413 (1992).
6. Schädel, M.: Radiochemical Studies of the Transactinide Elements. In: *Proceedings of the International School-Seminar on Heavy Ion Physics,* Dubna 1990, p. 84.
7. Hoffman, D. C.: Chemistry of the Transactinide Elements. In: *Proceedings of the Robert A. Welch Foundation Conference on Chemical Research XXXIV Fifty Years with Transuranium Elements*, Houston 1990, p. 255–274.
8. Türler, A., Gäggeler, H. W., Eichler, B., Jost, D. T., Kovacs, J., Scherer, U. W., Kadkhodayan, B., Gregorich, K. E., Hoffman, D. C., Kreek, S. A., Lee, D. M., Schädel, M., Brüchle, W., Schimpf, E., Kratz, J. V.: On-line Gas Chemistry Experiments with Transactinide Elements. In: *Proceedings of the International School-Seminar on Heavy Ion Physics,* Dubna 1993, p. 186.
9. Türler, A., Gäggeler, H. W., Gregorich, K. E., Barth, H., Brüchle, W., Czerwinski, K. R., Gober, M. K., Hannink, N. J., Henderson, R. A., Hoffman, D. C., Jost, D. T., Kacher, C. D., Kadkhodayan, B., Kovacs, J., Kratz, J. V., Kreek, S. A., Lee, D. M., Leyba, J. D., Nurmia, M. J., Schädel, M., Scherer, U. W., Schimpf, E., Vermeulen, D., Weber, A., Zimmermann, H. P., Zvara, I.: J. Radioanal. Nucl. Chem. **160**, 327 (1992).
10. Gäggeler, H. W.: J. Radioanal. Nucl. Chem. **183**, 261 (1994).
11. Hoffman, D. C.: Radiochim. Acta **61**, 123 (1993).
12. Kratz, J. V.: J. Alloys and Comp. **213/214**, 20 (1994).
13. Zvara, I., Chuburkov, Yu. T., Caletka, R., Zvarova, T. S., Shalaevsky, M. R., Shilov, B. V.: At. Energ. **21**, 8 (1966); J. Nucl. Energy **21**, 60 (1967); Sov. J. At. Energy **21**, 709 (1966).
14. Gäggeler, H. W., Jost, D. T., Baltensperger, U., Weber, A., Kovacs, A., Vermeulen, D., Türler, A.: Nucl. Instrum. Methods **A309**, 201 (1991).
15. Gäggeler, H. W., Jost, D. T., Kovacs, J., Scherer, U. W., Weber, A., Vermeulen, D., Türler, A., Gregorich, K. E., Henderson, R. A., Czerwinski, K. R., Kadkhodayan, B., Lee, D. M., Nurmia, M., Hoffman, D. C., Kratz, J. V., Gober, M. K., Zimmermann, H. P., Schädel, M., Brüchle, W., Schimpf, E., Zvara, I.: Radiochim. Acta **57**, 93 (1992).
16. Türler, A., Eichler, B., Jost, D. T., Piguet, D., Gäggeler, H. W., Gregorich, K. E., Kadkhodayan, B., Kreek, S. A., Lee, D. M., Mohar, M., Sylwester, E., Hoffman, D. C., Hübener, S.: to be submitted to Radiochim. Acta.
17. Zvara, I.: Radiochim. Acta **38**, 95 (1985).
18. Knacke, O., Kubaschewski, O., Hesselmann, K., (eds.): Thermochemical Properties of Inorganic Substances II, Springer-Verlag, Berlin 1991.
19. Morozov, A. I., Karlova, E. V.: Russ. J. Inorg. Chem. **16**, 12 (1971).
20. Domanov, V. P., Zin, Kim U.: Radiokhimiya **31**, 19 (1989).
21. Eichler, B.: Radiochim. Acta **72**, 19–26 (1996).
22. Zvara, I., Chuburkov, Yu. T., Belov, V. Z., Buklanov, G. V., Zakhataev, B. B., Zvarova, T. S., Maslov, O. D., Caletka, R., Shalaevsky, M. R.: J. Inorg. Nucl. Chem. **32**, 1885 (1970).
23. Eichler, B., Domanov, V. P., Zvara, I.: Report JINR, Dubna, **P12-9454** (1976).
24. Glebov, V. A., Kasztura, L., Nefedov, V. S., Zhuikov, B. L.: Radiochim. Acta **46**, 117 (1989).
25. Johnson, E., Fricke, B., Keller Jr., O. L., Nestor Jr., C. W., Tucker, T. C.: J. Chem. Phys. **93**, 8041 (1990).
26. Johnson, E., Fricke, B.: J. Phys. Chem. **95**, 7082 (1991).
27. Fricke, B., Johnson, E., Martinez-Rivera, G.: Radiochim. Acta **62**, 17 (1993).
28. Pershina, V., Fricke, B., Ionova, G. V., Johnson, E.: J. Phys. Chem. **98**, 1482 (1994).
29. Pershina, V., Sepp, W.-D., Fricke, B., Kolb, D., Schädel, M., Ionova, G. V.: J. Chem. Phys. **97**, 1116 (1992).
30. Zhuikov, B. L., Glebov, V. A., Nefedov, V. S., Zvara, I.: J. Radioanal. Nucl. Chem. **143**, 103 (1990).
31. Ryzhkov, M. V., Gubanov, V. A., Zvara, I.: Radiochim. Acta **57**, 11 (1992).
32. Pershina, V., Fricke, B.: J. Phys. Chem. **98**, 6468 (1994).
33. Pershina, V., Sepp, W.-D., Fricke, B., Rosén, A.: J. Chem. Phys. **96**, 8367 (1992).
34. Eichler, B., Türler, A., Gäggeler, H. W.: PSI Condensed Matter Research and Material Sciences Progress Report 1994, Annex IIIA Annual Report, Villigen 1995, p. 77.
35. Eichler, B.: PSI Condensed Matter Research and Material Sciences Progress Report 1993, Annex IIIA Annual Report, Villigen 1994, p. 93.
36. Zvara, I., Chuburkov, Yu. T., Tsaletka, R., Shalaevskii, M. R.: Radiokhimiya **11**, 163 (1969); Sov. Radiochem. **11**, 161 (1969).
37. Zvara, I., Belov, V. Z., Chelnokov, L. P., Domanov, V. P., Hussonois, M., Korotkin, Yu. S., Schegolev, V. A., Shalaevsky, M. R.: Inorg. Nucl. Chem. Lett. **7**, 1109 (1971).
38. Ghiorso, A., Nurmia, M., Eskola, K., Eskola, P.: Phys. Lett. **32B**, 95 (1970).
39. Ghiorso, A., Nurmia, M., Eskola, K., Eskola, P.: Phys. Rev. **C4**, 1850 (1971).
40. Kratz, J. V., Gober, M. K., Zimmermann, H. P., Schädel, M., Brüchle, W., Schimpf, E., Gregorich, K. E., Türler, A., Hannink, N. J., Czerwinski, K. R., Kadkhodayan, B., Lee, D. M., Nurmia, M. J., Hoffman, D. C., Gäggeler, H., Jost, D. T., Kovacs, J., Scherer, U. W., Weber, A.: Phys. Rev. **C45**, 1064 (1992).
41. Kadkhodayan, B., Türler, A., Gregorich, K. E., Nurmia, M. J., Lee, D. M., Hoffman, D. C.: Nucl. Instrum. Methods **A317**, 254 (1992).
42. Eichler, B., Türler, A., Jost, D. T., Gäggeler, H. W.: PSI Condensed Matter Research and Material Sciences Progress Report 1993, Annex IIIA Annual Report, Villigen 1994, p. 97.
43. Hoffman, D. C., Lee, D. M., Ghiorso, A., Nurmia, M. J., Aleklett, K., Leino, M.: Phys. Rev. **C24**, 495 (1981).
44. Zin, Kim U., Timokhin, S. N., Zvara, I.: Isotopenpraxis **24**, 30 (1988).
45. Bruchertseifer, F., Türler, A., Eichler, B., Gäggeler, H. W., Jost, D. T.: PSI Condensed Matter Research and Material Sciences Progress Report 1993, Annex IIIA Annual Report, Villigen 1994, p. 105.
46. von Dincklage, R. D., Schrewe, U. J., Schmidt-Ott, W. D., Fehse, H. F., Bächmann, K.: Nucl. Instrum. Methods **176**, 529 (1980).
47. Eichler, R., Eichler, B., Gäggeler, H. W.: PSI Condensed Matter Research and Material Sciences Progress Report 1992, Annex IIIA Annual Report, Villigen 1993, p. 99.
48. Kadkhodayan, B.: On-Line Gas Chromatographic Studies of Rutherfordium (Element 104), Hahnium (Element 105), and Homologs, Ph. D. Thesis, **LBL 33961** (1993).
49. Rudolph, J., Bächmann, K.: Microchim. Acta **I**, 477 (1979).
50. Rudolph, J., Bächmann, K.: J. Radioanal. Chem. **43**, 113 (1978).
51. Rudolph, J., Bächmann, K.: Radiochim. Acta **27**, 105 (1980).

52. Türler, A., Gregorich, K. E., Hoffman, D. C., Lee, D. M., Gäggeler, H. W.: PSI Condensed Matter Research and Material Sciences Progress Report 1991, Annex III Annual Report, Villigen 1992, p. 68.
53. Eichler, B., Reetz, T., Domanov, V. P.: Report JINR, Dubna, **P12-20047** (1976).
54. Zvara, I., Timokhin, S. N., Chuburkov, Yu. T., Domanov, V. P., Gorski, B.: Joint Institute for Nuclear Research, Laboratory for Nuclear Reactions, Scientific Report 1989–1990, **E7-91-75**, Dubna 1991, p. 34.
55. Gäggeler, H. W.: Reaktionsmechanismen zur Synthese schwerster Elemente aus Schwerionenreaktionen, PSI-Bericht **Nr. 14**, Villigen 1988.
56. Nai-Qi, Ya, Jost, D. T., Baltensperger, U., Gäggeler, H. W.: Radiochim. Acta **47**, 1 (1989).
57. Gäggeler, H., Jost, D., Baltensperger, U., Nai-Qi, Ya, Gregorich, K. E., Gannett, C. M., Hall, H. L., Henderson, R. A., Lee, D. M., Leyba, J. D., Nurmia, M. J., Hoffman, D. C., Türler, A., Lienert, C., Schädel, M., Brüchle, W., Kratz, J. V., Zimmermann, H. P., Scherer, U. W.: First results from gaschemistry experiments with hahnium, PSI-Bericht **Nr. 49**, Villigen 1989.
58. Jost, D. T., Vermeulen, D.: IEEE Trans. Nucl. Sci. **39**, 186 (1992).
59. Türler, A., Gäggeler, H. W., Eichler, B., Jost, D. T., Kovacs, A., Vermeulen, D., Kadkhodayan, B., Gregorich, K. E., Kreek, S. A., Lee, D. M., Hoffman, D. C., Baisden, P., Kratz, J. V., Becker, H.-U., Gober, M. K., Zimmermann, H. P., Schädel, M., Brüchle, W., Jäger, E., Pershina, V., Schausten, B., Schimpf, E.: PSI Condensed Matter Research and Material Sciences Progress Report 1992, Annex IIIA Annual Report, Villigen 1993, p. 95.
60. Gregorich, K. E., Hall, H. L., Henderson, R. A., Leyba, J. D., Czerwinski, K. R., Kreek, S. A., Kadkhodayan, B. A., Nurmia, M. J., Lee, D. M., Hoffman, D. C.: Phys. Rev. **C45**, 1058 (1992).
61. Gregorich, K. E.: Nucl. Instrum. Methods **A302**, 135 (1991).